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Three-dimensional simulation of hexagonal phase of a *specific* polymer system under shear: The dynamic density functional approach

A. V. M. Zvelindovsky, B. A. C. van Vlimmeren, G. J. A. Sevink, N. M. Maurits, and J. G. E. M. Fraaije
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The first three-dimensional (3D) simulation of meso-phase formation in a specific polymer system—55% aqueous solution of the triblock polymer surfactant $(EO)_{13}(PO)_{30}(EO)_{13}$—under simple steady shear is performed. The method is based on dynamic mean-field density functional theory. The hexagonal phase is investigated. The simulations reproduce recent experimental observations on the same polymer system. © *1998 American Institute of Physics.* [S0021-9606(98)51744-8]

Because of the wide area of industrial applications the behavior of complex polymer liquids under shear is an intensively studied topic both experimentally and theoretically.[1–7] The concentrated aqueous mixtures of amphiphilic block copolymers are of special interest as they are intermediate between polymer melts and aqueous solutions of low molar mass surfactants.[8]

The hexagonal phase is one of the mesophases known in melts and solutions of triblock copolymers. Phase transitions in such systems and the influence of external flow on them have been the subject of theoretical and experimental studies during many years[9,10] and remains ''a hot topic'' due to classes of materials like polymer surfactant solutions.[8,11]

During the last couple of years the time evolution of morphologies in complex liquids in external flows has been studied by computer simulation techniques using time-dependent Landau–Ginzburg models.[1,12–15] These models are based on traditional free energy expansion methods[16–18] which contain only the basic physics of phase separation[19] and are not well suited for specific applications. In contrast to these phenomenological theories we do not truncate a free energy expansion, but retain the full polymer path integral by a numerical procedure.[19–25] Very recently Kawakatsu and Doi started to use a similar approach.[26,27] The benefit of such an approach is that it allows for the description of the mesoscopic dynamics of a *specific* complex polymer liquid.

Recently[6] we have simulated the lamellar system of model diblock copolymer melt A_8B_8 under shear in 3D. To our knowledge no simulations of polymer morphology formation (either with or without shear) in 3D for a *specific* system have been reported.

Here we have simulated the behavior of 55% aqueous solution of the triblock polymer surfactant $(\text{Ethylene Oxide})_{13}(\text{Propylene Oxide})_{30}(\text{Ethylene Oxide})_{13}$ (Pluronic L64[8,11]) under simple steady shear. Very recently, experiments on the same system have been carried out.[8] Our results give a vivid demonstration of the dynamics of the 3D morphologies that is complementary to the experimental observations.

The aqueous Pluronic L64 solution is modeled as a compressible system consisting of ideal Gaussian chain molecules in a mean-field environment. The free energy is a functional of a set of particle concentrations $\{\rho\}$[20,21]

$$F[\{\rho\}] = -kT \ln \frac{\Phi_p^{n_p} \Phi_s^{n_s}}{n_p! n_s!} - \sum_I \int_V U_I(\mathbf{r}) \rho_I(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \sum_{I,J} \int_{V^2} \epsilon_{IJ}(\mathbf{r}-\mathbf{r}') \rho_I(\mathbf{r}) \rho_J(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + \frac{\kappa_H}{2} \int_V \left(\sum_I \nu_I (\rho_I(\mathbf{r}) - \rho_I^0) \right)^2 d\mathbf{r} \quad (1)$$

where n_p (n_s) is the number of polymer (solvent) molecules, Φ is the intramolecular partition function, I is a component index (EO, PO, or solvent) and V is the system volume. The external potential U_I is conjugate to the particle concentration ρ_I via the Gaussian chain density functional.[20] The average concentration is ρ_I^0 and ν_I is the particle volume. The cohesive interactions have kernels ϵ_{IJ}.[20] The Helfand compressibility parameter is κ_H.[21]

The dynamics of the system is governed by the diffusion-convection equation with sheared periodic boundary conditions as described in Ref. 6. The dynamic equations are closed by the expression for the free energy (1) and the Gaussian chain density functional.[20] In this approximation the phase separation dynamics is affected by flow via the convection term in Landau–Ginzburg type evolution equation. Eight dimensionless parameters enter the numerics: three exchange parameters $\chi_{IJ} \equiv (\beta/2\nu)[\epsilon_{IJ}^0 + \epsilon_{JI}^0 - \epsilon_{JJ}^0 - \epsilon_{II}^0]$, the dimensionless time $\tau \equiv kTMh^{-2}t$ (h is the mesh-size), a noise scaling parameter Ω ($\Omega = 100$ in the simulation),[23] the grid scaling $d \equiv ah^{-1} = 1.1543$ (a is the Gaussian chain bond length[24]), the compressibility parameter $\kappa' \equiv \beta \kappa_H \nu = 10$ and the shear rate[6,7] $\tilde{\dot{\gamma}} = \Delta t \dot{\gamma} = 10^{-3}$, the same value as used in Ref. 1. For simplicity we use identical mobility coefficients and particle volumes for all components.

From comparison of random phase approximation (RPA)[29] and molecular force-field single chain structure fac-

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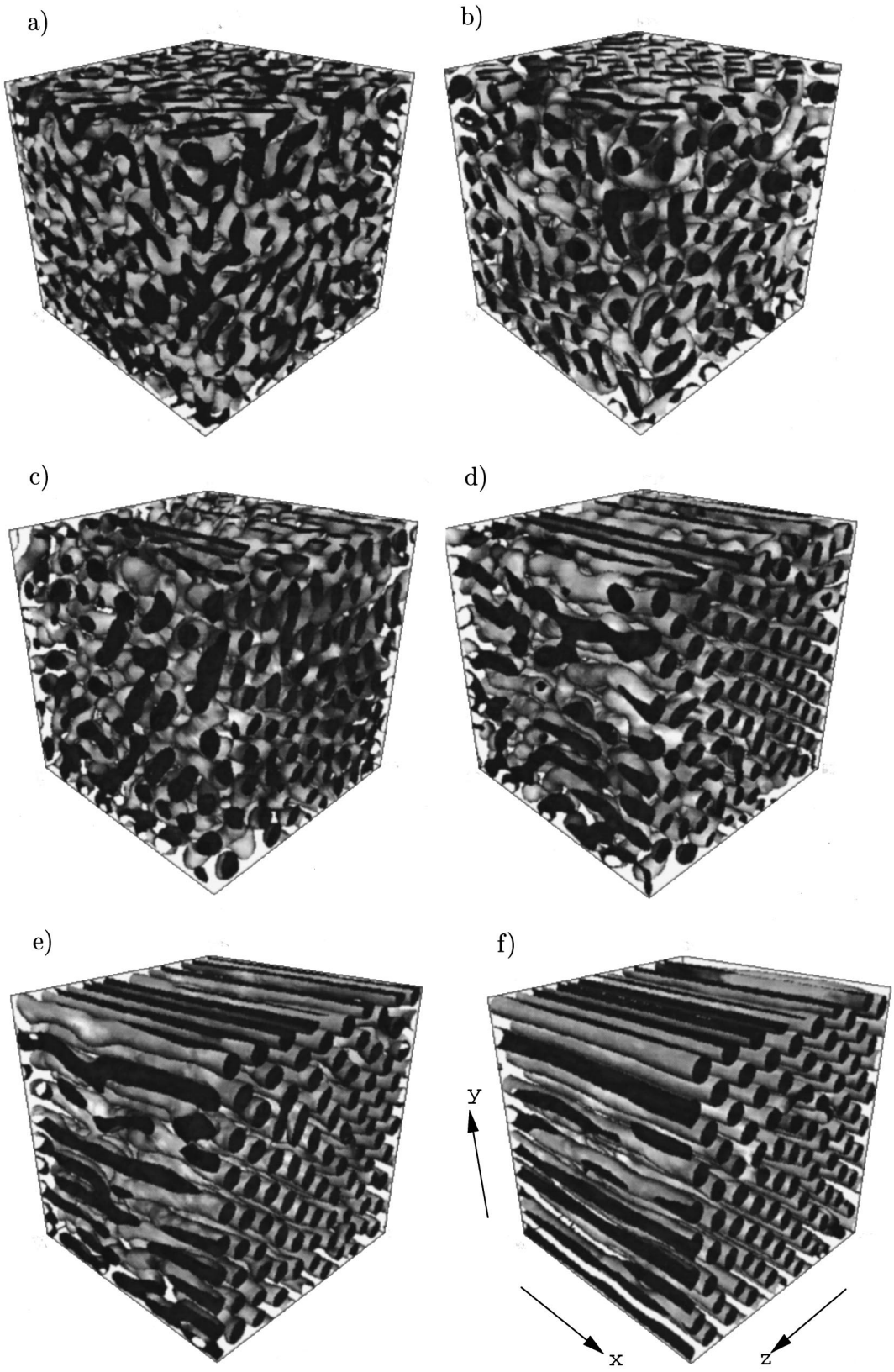

FIG. 1. Mesophases of 55% Pluronic L64 in water at different times τ: 250 (a), 5000 (b), the start of shear, 6250 (c), 7500 (d), 8750 (e), 12500 (f). The isosurfaces are at $\theta_P \equiv \nu_P \rho_P = 0.33$. Shear is the same for Figs. (b)–(f): x axis is in velocity direction, y axis is in velocity gradient direction, and z axis is the neutral one.

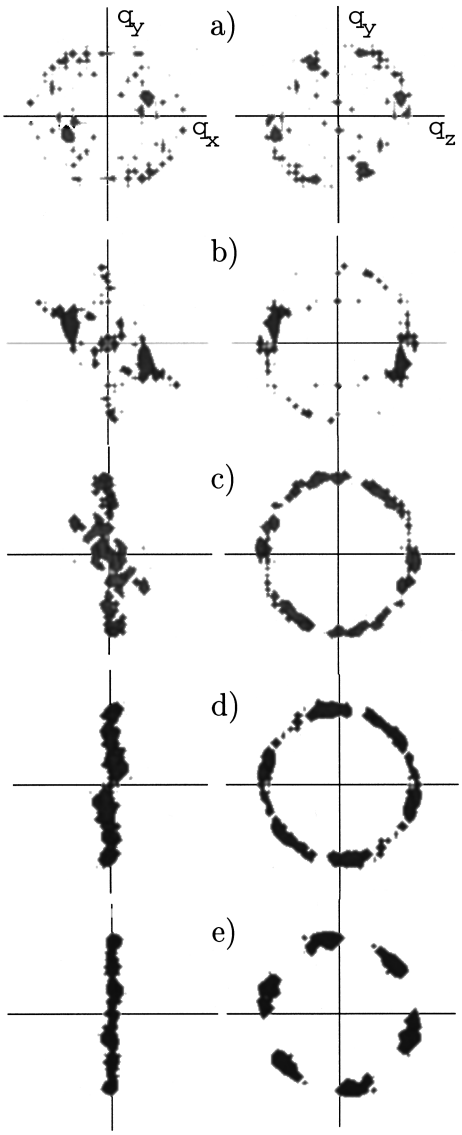

FIG. 2. Projections of 3D structure factor of morphologies from Figs. 1(b)–1(f) on the xy (left) and yz plane (right): τ=5000 (a), 6250 (b), 7500 (c), 8750 (d), 12500 (e). Isosurface of the 3D structure factor is at $|\tilde{\theta}_P(\mathbf{q})| = 10.0$.

tors (generated by Monte Carlo), we found that the structure factor is well represented by an $E_3P_9E_3$ Gaussian chain,[28] which corresponds to 3 to 4 monomers per bead. The solvent molecule is represented as a single bead.

The solvent–polymer interaction parameters were calculated from vapor pressure data of aqueous homopolymer solutions,[30] using the Flory–Huggins expression[31] $\chi_{IJ} = \theta^{-2}\{\ln p/p^0 - \ln(1-\theta) - (1-1/N)\,\theta)\}$, where p is the vapor pressure and θ is the polymer volume fraction. The chain length N was determined using $\frac{13}{3}$ (EO) or $\frac{30}{9}$ (PO) monomers per bead. This gives for the interaction parameters $\chi_{ES} = 1.4$, $\chi_{PS} = 1.7$ (here S denotes solvent). For the EO–PO interaction parameter from group contribution methods[32] we estimated $\chi_{EP} = 3.0$.

We have simulated the time evolution of the Pluronic-water mixture in a cubic box $64\times64\times64$. The simulation was started from the homogeneous solution. In Fig. 1(a) the

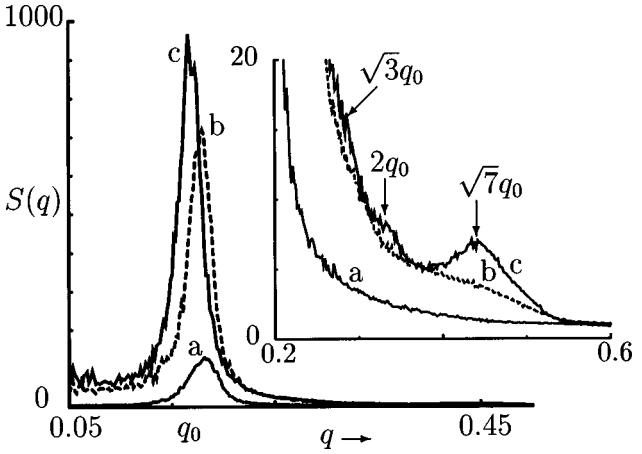

FIG. 3. The angle averaged structure factor $S(q)$ of morphologies with no shear applied at τ=250, Fig. 1(a) (a), τ=500 (b), and τ=5000, Fig. 1(b) (c).

morphology at τ=250 is shown. In the initial stage of the microphase separation the system exhibits no regular structure. However, the observed domains already have the characteristic size typical for this triblock copolymer system.

In Fig. 1(b) the morphology at the start of shear (τ =5000) is shown. The system consists of different imperfect clusters of hexagonally packed cylinders with a lot of defects. The angle averaged structure factor of this morphology has peaks at $2q_0$ and $\sqrt{7}q_0$, where $q_0 = 0.17h^{-1}$ is the frequency of the primary peak (Fig. 3). This indicates the presence of a hexagonal structure before shear is applied. The expected peak at $\sqrt{3}q_0$ is still hidden in the broad shoulder of the primary peak. Projections of the 3D structure factor onto two different directions [Fig. 2(a)] consist of rings of primary maxima from local hexagonal clusters with some preferred orientation, but without predominant global ordering. Comparison of the simulated and experimental[11] structure factors gives an estimate for the Gaussian bond length a = 1.8 nm. The time evolution of the structure factor before shear is applied is shown in Fig. 3. The primary peak shifts in time to lower frequencies and its height increases. Appearing of secondary peaks indicates formation of hexagonal structure which slowly improves in time even without shear.

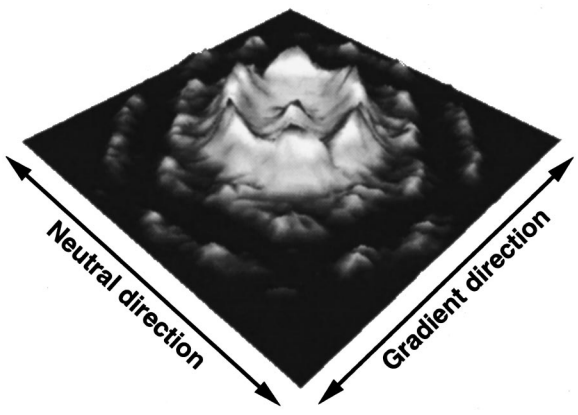

FIG. 4. Logarithm of 3D structure factor summed in x-direction for final structure in Fig. 1(f).

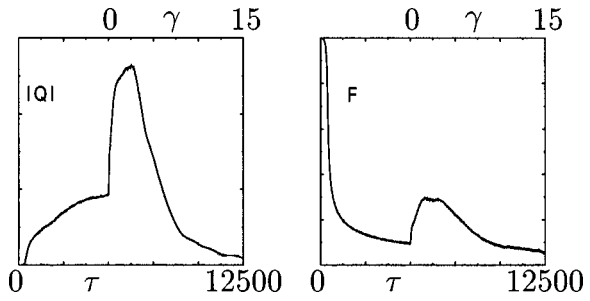

FIG. 5. The anisotropy factor Q and the free energy F as functions of time and shear strain γ (indicated on top). The start of shear is at $\gamma=0$ or $\tau=5000$.

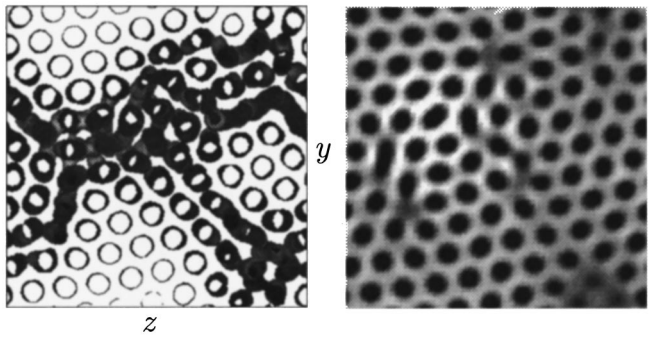

FIG. 6. A view through (left) the morphology from Fig. 1(f) and a yz-orthoslice (right) of the same morphology.

Applying of simple steady shear changes the picture drastically. The free energy (Fig. 5) increases immediately after switching on the shear flow at $\tau=5000$ and then slowly decreases while the system finds a path to a new morphology. The volume averaged anisotropy factor $Q=\langle\nabla_x\rho\nabla_y\rho\rangle_V$, which is related to the stress tensor,[3,25] is a convenient measure for the anisotropy of the morphology and reordering process due to shear flow.[6]

The increase of Q from $\tau=0$ to $\tau=5000$ (Fig. 5) corresponds to the formation of more and more sharp boundaries. Note, that the system is never completely isotropic due to periodicity imposed by the simulation box. In the initial stages of shear the reordering proceeds via breakup of the structures [Fig. 1(c)], which leads to an increase in free energy and to an increase of the anisotropy factor. The pieces are tilted in the direction of flow. Then the oblong micelle-like structures coalescence [Fig. 1(d)] to form new cylinders which align in the direction of shear. This reorientation is reflected in the rapid decrease in the anisotropy factor (Fig. 5). The alignment process is clearly observed in the projections of 3D structure factor, Figs. 2(b) and 2(c). The yx-projection is squeezed into a line and the yz-projection forms a circle. The position of primary peak remains the same during shearing (Fig. 2).

The characteristic features of the last stage of reorientation are defect annihilation [Figs. 1(e) and 1(f)] and reordering of hexagonal clusters [Figs. 2(d) and 2(e)]. Initially there are many hexagonal clusters with different orientations, which corresponds to the ring in Fig. 2(d). In the final stage the system forms a few big clusters with nearly the same orientation [Figs. 2(e), 4, and 6]. Hexagonal ordering is especially clear from logarithm of structure factor in Fig. 4, which makes visible peaks of second and third order. The heights of the peaks increase slowly with improving the structure in time. The view through and the cut of the morphologies, e.g., Fig. 6, illustrate the process of forming a global hexagonal lattice which is somewhat similar to crystal growth. Very recent experiments on the same Pluronic surfactant solution (with almost the same concentration—53%) demonstrate exactly the same alignment of cylinders in the direction of flow as in our simulation. The 10 plane of the hexagonal lattice is experimentally found to be parallel to the shear plane.[8] Our simulation gives the orientation of the main cluster that is 10° off [Figs. 2(e) and 6]. The tendency of the simulation is towards perfect structure. Note, that for another triblock copolymer system[10] the perpendicular lattice orientation was found together with the same orientation of cylinders along the flow.

We conclude that it is possible to apply the dynamic mean-field density functional method to predict the mesophase formation of specific polymer systems under shear.

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